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POYNUCLEAR AROMATIC HYDROCARBONS IDENTIFICATION

USING GC/FT-IR AND PAIRS

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ABSTRACT

Gas chromatography/Fourier transform infrared (GC/FT-IR) spectra of 33 polynuclear aromatic hydrocarbons (PAHs) have been measured at the Ontario Ministry of the Environment. High signal to noise ratio (SNR) vapor phase spectra have been obtained for the majority of the PAHs, a lower SNR being obtained for 4 PAHs with very low vapor pressures. A vapor phase infrared spectral library has been created which makes the identification of PAH target compounds possible by GC/FT-IR. The spectral region 700 to 1000 cm^{-1} containing the C-H and $-\text{CH}_2$ out-of-plane and C-C in-plane bending modes demonstrate a unique spectral feature for each PAH. It is possible to distinguish between a group of PAH isomers using only the information from this spectral region. The PC based version of the program for the Analysis of InfraRed Spectra (PAIRS*) is employed and an interpretation tree specific for PAHs is at the preparation stage to make "functional group frequency" screening of PAHs possible.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are a major class of chemical compounds with extremely complex structures. Due to large variability in isomer formation several hundred different types of PAHs can exist. For example, for PAHs containing 6 aromatic rings, 82 isomeric configurations are possible. Since the toxicity, carcinogenicity, and mutagenicity of different PAH isomers can be very different, the ability to distinguish these isomers for environmental assessment and consequently, for remedial actions is important. The Ontario Ministry of the Environment (MOE) has been analyzing 37 targeted PAHs at the Trace Organics Section (TOS) of the Laboratory Services Branch (LSB)⁽¹⁾. These PAHs had been selected based on their occurrence in the province of Ontario. The spectra of only 13 of these 37 PAHs are in the Nicolet/Aldrich enhanced U.S. Environmental Protection Agency infrared vapor phase library

(EPA library)⁽²⁾. The lack of the other 24 PAH spectra in the EPA library complicates the identification of the gas chromatograph/Fourier transform infrared spectra (GC/FT-IR) of these PAHs.

The applicability of gas chromatography/Fourier transform infrared spectroscopy (GC/FT-IR) to environmental sample analysis containing some PAHs has been demonstrated by several groups⁽³⁻⁵⁾. In these studies only a few of the PAHs listed in Table 1 have been investigated. The use of the combined data from GC/FT-IR and GC/MS for sample analysis has also been demonstrated^(6,7), and data obtained from directly linked GC/FT-IR/MS have been reported⁽⁸⁾. These studies have demonstrated the need for vapor phase infrared spectral data bases that include PAHs containing four or higher aromatic rings⁽⁹⁾. The use of GC/MS for identification of PAHs is a powerful technique for obtaining molecular structural information but most conventional electron impact ionization mass spectrometers (EI/MS) can lead to identical fragmentation of isomers and thus to identical mass spectra. Matrix isolation infrared spectrometry (MI-IR) has also been applied for PAH identification^(9,10), in mixtures containing up to 5 components and gas chromatography matrix isolation (GC/MI-IR) spectra of several PAHs have been recorded⁽¹¹⁾. The quality of MI-IR spectra is dependent on the type of matrix used and the ratio of matrix to sample. Both these factors can cause infrared band splitting and band shifts and can change full width at half height (FWHH) of some bands.

In order to increase our capability for identification of PAHs and in order to distinguish between their many isomeric configurations we have measured the GC/FT-IR spectra of 33 PAHs and created a vapor phase infrared spectral library. These spectra reveal that the spectral region from 700 to 1000 cm^{-1} containing the aromatic C-H and $-\text{CH}_2$ out-of-plane and C-C in-plane bending modes can provide unique information for each isomeric compound.

EXPERIMENTAL

A. CHEMICALS.

Solutions of PAHs were prepared by dissolving 1-2 mg of each standard in 1 ml of

toluene. Benzo[a]anthracene, benzo[b]anthracene (80% purity (UV)), benzo[a]fluorene (>98% (HPLC)), benzo[ghi]perylene, coronene (97% (HPLC)), 9,10-dimethyl anthracene (97% (HPLC)), dibenzo[a,c]anthracene (>97% (UV)), dibenzo[a,h]anthracene, 7,12-dimethylbenz[a]anthracene, 2-methyl anthracene (>99% (HPLC)), triphenylene (>98% (HPLC)) and Perylene (>99% (HPLC)) were purchased from Fluka AG, chem.Fabrik. Benzo[c]phenanthrene (Community Bureau of References), anthracene (Aldrich, 99.9%), benzo[a]pyrene (Aldrich, 98%), benzo[b]fluoranthene (Supleco, Inc.), and benzo[k]fluoranthene (Supleco, Inc. 99%) were also used for sample preparations. 9-Methyl anthracene, 3-methyl cholanthrene, O-terphenyl, M-terphenyl and P-terphenyl were obtained from Eastman Kodak Co. and acenaphthene, acenaphthylene, fluorene, fluoranthene, and phenanthrene were obtained from EPA Research Triangle Park.

B. INSTRUMENTATION

A Nicolet 5SX (Madison, WI) FT-IR spectrometer equipped with a 0.1 mm HgCdTe cryogenic detector and an air cooled nichrome wire source was used to measure the GC/FT-IR spectra. A Hewlett-Packard 5890 (Palo Alto, CA) gas chromatograph equipped with a splitless injector, a wide bore column (cross-linked methyl Silicon Gum, 25m x 0.32mm x 0.17 micrometer film thickness) and a flame ionization detector were used for the separation. The dimensions of the GC/FT-IR light pipe interface used were 12 cm x 0.1 cm. Using the above combination, interferograms were collected at a sampling rate of 50 kHz and an optical retardation of 0.125 cm. Either the Gram-Schmidt orthogonalization or the ChemiGram methods were used to reconstruct a real time chromatogram from the interferogram and the low resolution infrared spectra⁽¹²⁾. At the end of the experiment the appropriate number of the interferograms were coadded and Fourier transformed to obtain the infrared spectrum of each compound.

For the preliminary analyses of PAHs the LSB routine method PAAPAH-AC8NCQ.21⁽¹⁾ was used. This resulted in obtaining GC/FT-IR spectra of low signal-to-noise ratio (SNR). This method was modified in several ways to enhance the spectral SNR. A wide bore column was used to make an injection of a higher volume of the sample possible. We also employed

on-column injection instead of split injection without masking the lower boiling PAHs (e.g. tetralin and naphthalene) under the solvent band and no make up gas was used to prevent analyte dilution in the light pipe.

The signal of the cryogenic Hg-Cd-Te detector decreases with increasing temperature of the light pipe. This phenomenon is attributed to (1) the temperature induced changes in the reflectivity of the gold coating inside the light pipe and (2) the masking of the modulated infrared signal from the interferometer by the unmodulated thermal radiation from the light pipe. For our detector, we observed a loss of about 45% of the signal by increasing the light-pipe temperature from 50 to 290°C. The boiling points of the PAHs can vary from approximately 200 to 600°C. Hence, the light pipe had to be operated at its optimum temperature which is about 285°C throughout our investigation. This represents a loss of about 45% of signal intensities in our experiments.

RESULTS

The sensitivity of the GC/FT-IR was first evaluated using the following experimental conditions. The light pipe temperature was set at 280°C, the column head pressure was varied from 5 to 20 psi and the GC/FT-IR spectra of a solution of dimethyl phthalate (DMP) in toluene was recorded. For 60-nanogram DMP injected at a column head pressure of 15 psi, we could achieve a SNR of 10 for the most intense band in the spectrum. Lower detection limits have been reported in the literature, but the operating conditions have been very different in those studies. The light pipe temperature in those cases has been set between 170 to 240°C. From the relationship between the signal of the detector and the light pipe temperature it becomes clear that we will have a detection limit of 30 nanogram if we use a light pipe temperature of about 200°C.

In the preliminary work the vapor phase spectra of 10 PAHs were collected. These 10 PAHs are among the 13 PAHs for which vapor phase spectra exist in the EPA library. The

temperature of the light pipe and the transfer line were set at 285°C, and the GC was temperature programmed from 80 to 300°C with an initial two minutes hold at 80°C. The GC oven temperature was ramped at a rate of 8 to 20°C/min, depending on the type of the sample, to 300°C. The quality of our spectra were either equivalent or in some instances, superior to those in the EPA library. Table 1 gives the list of these compounds (numbers 1 to 10). Under the same experimental conditions we obtained the GC/FT-IR spectra of the other PAHs (compounds number 11 to 33). The spectrum of each compound was measured at least three times to obtain the best quality possible. When necessary, solutions were concentrated by evaporating some of the solvent. Attempts to obtain the infrared spectra for Picene and Coronene were unsuccessful. Picene has a very low solubility in toluene or any other organic solvent at room temperature. Coronene has an estimated boiling point of about 590°C. Chrysene, Dibenzo[a,h]Anthracene, Perylene and Benzo[ghi]Perylene have relatively lower solubility than other PAHs in organic solvents which resulted in obtaining spectra with lower SNR.

These spectra have been transferred from the Nicolet 620 computer to the MS/DOS system in the Spectral Calc format, Thus forming part of the Ontario Ministry of the Environment vapor phase infrared spectral library of the PAH standards. This library will be expanded with other types of PAHs such as alkyl and halogen substituted, nitro-PAHs and heteroatom containing PAHs.

The creation of this library allowed us to attempt to identify the components of a mixture. The experimental condition were as before except for the use of a DB-5 25m x 0.33 i.d. x 1.0 micrometer film thickness capillary column. A sample of standard solution of PAHs mixture (3 microliters) was injected into the GC column and a GC/FT-IR analysis was carried out. Figure 1 shows the out put obtained from FID and the Gram-Schmidt reconstructed chromatograph for this analysis. After Fourier transformation of the interferograms the spectra were searched using the EPA library which has a total of 5010 entries. For those components whose infrared spectra are in the library, the correct identification was provided. For eight components for which there is no vapor phase spectra in the library, four best matches were given, all of which were

incorrect. We were able, however, to identify correctly these PAHs using the newly created library. This experiment emphasizes the importance of creating an MOE library of PAH infrared spectra which enables the identification of the target PAHs encountered in the province of Ontario.

DISCUSSION AND CONCLUSION

Table 1 lists the PAHs investigated in the current study and the infrared absorption bands with significant intensities in the region 650 to 4000 cm^{-1} . Figure 2 shows the GC/FT-IR spectra of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[b]pyrene and perylene, five PAH isomers with five rings and molecular weight of 252.3, in the spectral region 650 to 4000 cm^{-1} . Several changes in the appearance of infrared spectra, such as frequency shifts and changes in the relative intensities, are associated with changes in the physical state of a compound. For example, the infrared bands associated with the C-H aromatic stretching shift toward higher frequencies and those associated with C-H out-of plane bending modes often shift toward lower frequencies as the state of the matter changes from condensed to vapor state. Also, some active modes in the spectra of the condensed phase become inactive in the gas phase or show a considerable decrease in intensity. This is observed for the most of the vibrational modes associated with C-H in plane bending and CC stretching modes. The simplicity of the vapor phase spectra (see Figure 2) could be considered advantageous for fast identification of the components of a complex environmental sample mixture.

While we are in the process of accumulating more vapor phase infrared spectra to enhance our capability for identification of the PAHs, it is also recognized that due to the large variability of PAHs which can be present in complex environmental sample mixtures other methods for fast identification must be explored. Program for the Analysis of InfraRed Spectra (PAIRS) which was originally developed by Woodruff and Smith ⁽¹³⁾, has been implemented recently in our laboratory on a 386 based personal computer running MS/DOS ⁽¹⁴⁾. The information flow in

PAIRS* is similar to the reasoning a chemist uses in interpreting spectral data. The computerized interpreter requires as input the spectrum, supplemental information and interpretation rules. As output, the program prints probabilities for each functional group under consideration. We have used PAIRS* to interpret the PAHs listed in Table 1 with different degrees of success. The result of analysis using PAIRS* to identify triphenylene is given as an example in Table 2. It is interesting to note that the strongest infrared absorption peak for triphenylene and for thiophene are positioned at 737 and 714 cm^{-1} respectively. Since PAIRS* interprets each spectrum based on peak locations, peak intensities, and peak widths, and since at this time we have not incorporated the interpretation tree for the PAHs the most probable functionality was interpreted as thiophene. The next two probabilities i.e., aromatic and aromatic 1,2-substituted seem reasonable conclusion for triphenylene. At the time of writing this manuscript we are in the process of writing and testing an interpretation tree for PAHs in the vapor state. It is hoped that this interpretation tree for PAHs can make the "functional group frequency" screening of PAHs possible.

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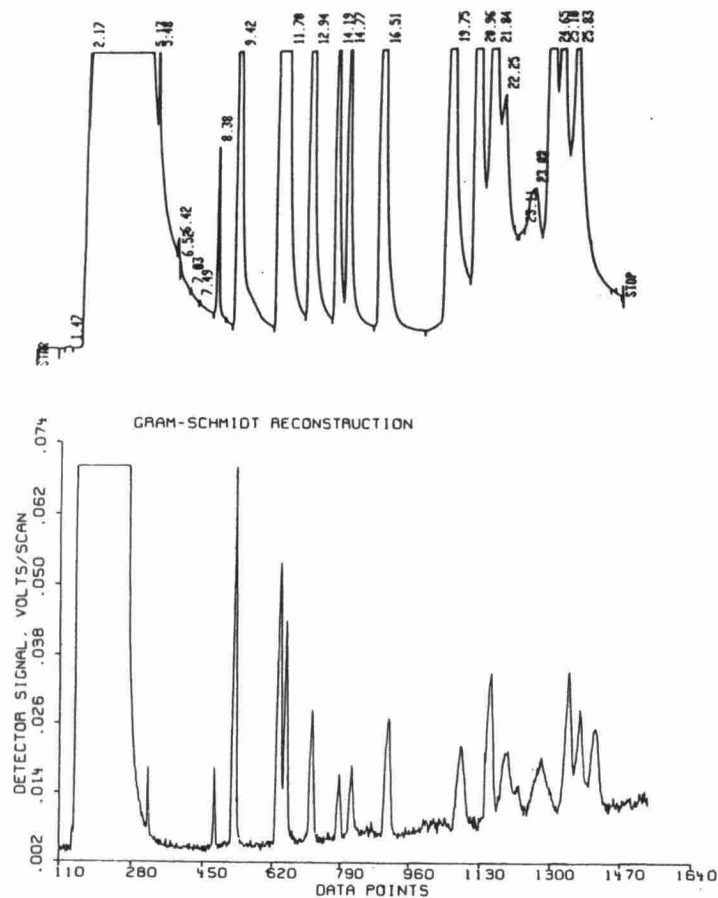


Figure 1- The gas chromatograph and the Gram-Schmidt reconstructed chromatograph from the analysis of a mixture of PAHs standard solution.

Table 1- The infrared absorption bands for PAHs in the spectral region 650 to 4000 cm^{-1} (The peak with the highest intensity in each spectrum is underlined).

1)Naphthalene	<u>779</u> , 1006, 1507, 3065
2)2-Chloronaphthalene	739, 806, <u>849</u> , 880, 943, 1074 1137, 1192, 1232, 1345, 1454, 1593, 1628, 3066
3)Anthracene	<u>724</u> , 874, 1538, 3063
4)Phenanthrene	<u>730</u> , 806, 860, 1037, 1239, 1454 1500, 3065
5)2-Methyl anthracene	733, 1457, 1536, 1636, 2874, 2931 <u>3057</u>
6)9-Methyl anthracene	<u>726</u> , 773, 829, 996, 1306, 1346 1386, 1524, 1689, 2888, 3062, 3082
7)Fluorene	<u>736</u> , 1001, 1177, 1412, 1453, 1481 2916, 3028, 3071
8)Acenaphthylene	722, <u>770</u> , 829, 859, 1084, 1148 1387, 1421, 1461, 1619, 1804, 1918 2946, 3063, 3100
9)Acenaphthene	<u>782</u> , 834, 1366, 1427, 1607, 2854 2898, 2940, 3054
10)O-Terphenyl	<u>700</u> , 748, 1009, 1067, 1437, 1473 1597, 3031, 3069
11)M-Terphenyl	699, <u>749</u> , 796, 893, 1026, 1404 1447, 1474, 1497, 1594, 3036, 3069
12)P-Terphenyl	697, 751, 838, 1007, <u>1482</u> , 1525 1598, 3034
13)1-Methyl phenanthrene	<u>744</u> , 799, 876, 1461, 1599, 2881 2938, 2978, 3064
14)Fluoranthene	741, <u>773</u> , 825, 1426, 1454, 3066
15)Pyrene	708, 740, <u>837</u> , 1182, 1432, 1596 1786, 3051
16)Benzo[a]fluorene	715, <u>753</u> , 813, 1016, 1469, 2906 3066

...continued

Table 1 - Continued...

17) Benzo[b]fluorene	723, 1306, 3024,	766, 1415, 3064	865, 1437,	953, 1473,	1017, 1503,	1188, 2914
18) Triphenylene	737,	1049,	1435,	1495,	3032,	3084
19) Chrysene	756, 3089	807,	858,	1030,	1424,	3066
20) Benzo[a]anthracene	744, 1500,	799, 1681,	880, 3062	1038,	1276,	1454
21) Benzo[c]phenanthrene	667, 1229,	744, 1417,	795, 1496,	832, 3014,	863, 3058	1030
22) Benzo[b]fluoranthene	740, 1599,	774, 3071	887,	1442,	1454,	1524
23) Benzo[k]fluoranthene	740, 1446,	771, 1611,	821, 3063	880,	1265,	1426
24) Benzo[a]pyrene	687, 1023,	741, 1079,	757, 1185,	821, 1263,	845, 3057	879
25) Benzo[e]pyrene	744,	766,	826,	1440,	3056,	3086
26) Perylene	767,	812,	1383,	1589,	3059,	3087
27) Indeno[1,2,3cd]pyrene	730,	837,	879,	1381,	1443,	3057
28) Benzo[ghi]perylene	752,	768,	841,	3055		
29) Dibenzo[a,c]anthracene	717, 3066,	755, 3077	877,	1432,	1493,	1508
30) Dibenzo[a,h]anthracene	739, 3077	801,	881,	1023,	1088,	1454
31) 9,10-Dimethyl anthracene	743,	1367,	1389,	2941,	3088	
32) 7,12-Dimethyl benz[a]anthracene	745,	805,	2934,	3073		
33) 3-Methylcholanthrene	742, 2929,	799, 3049	869,	1503,	2866,	2893

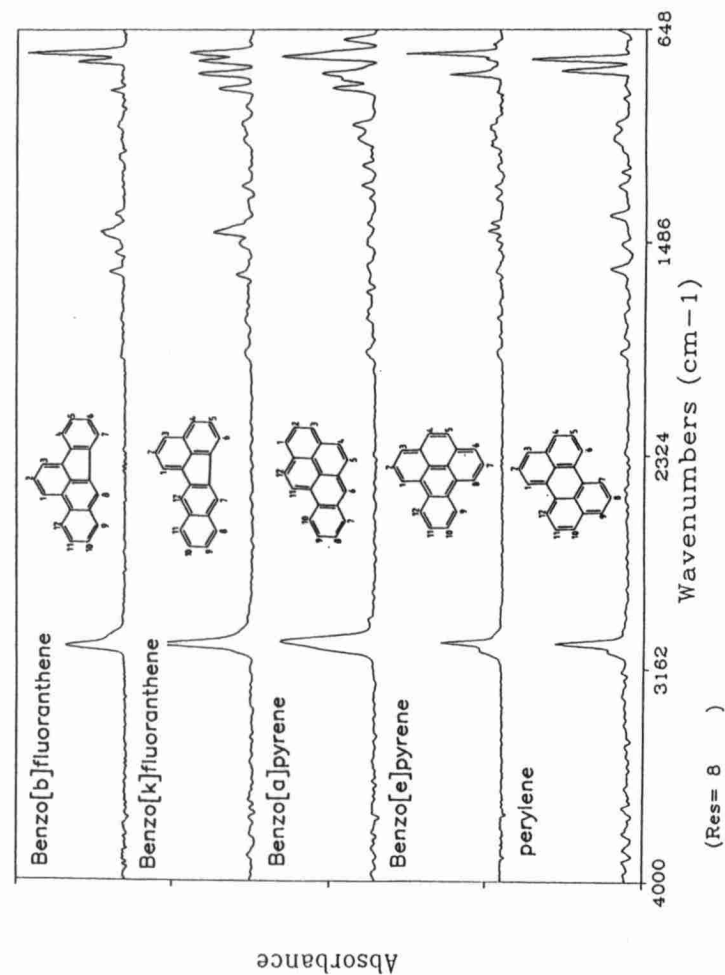


Figure 2- GC/FT-IR spectra for benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]pyrene and perylene.

Table 2- The final report from PAIRS+ for triphenylene.

The final report from the upgraded PAIRS:

Spectral data summary for:

TRIPHENELYNE

The solvent is: neat

No empirical formula given

There are	6 peaks
Line	Width Intensity Location
1	sharp 1 617
2	average 10 737
3	average 2 1435
4	average 1 1496
5	average 1 3032
6	average 3 3086

Printout is sorted by probability:

Group name	Probability
1) THIOPHENE	0.60
2) AROMATIC	0.55
3) AROM-1.2-SUBST	0.55
4) OLEFIN-(NON-AROM)	0.20
5) OLEFIN-CH2=CR2	0.20
6) OLEFIN-CHR=CR2	0.15
7) OLEFIN-CHR=CHR(T)	0.15
8) OLEFIN-CHR=CHR(C)	0.15
9) OLEFIN-CHR=CH2	0.13
10) FURAN	0.10
11) AROM-MONOSUBST	0.06
12) AROM-1.3-SUBST	0.06
13) HETEROAROMATIC	0.06
14) PYRIDYL	0.06
15) PYRAZYL	0.06
16) PYRIMIDYL	0.06
17) PURINE	0.06
18) INDOLE	0.06
19) PYRROLE	0.01
20) Z1	0.01